

## Chapter 10

# Electrochemiluminescence of Organometallics and Other Transition Metal Complexes

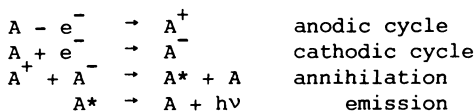
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A variety of transition metal complexes including organometallics was subjected to an ac electrolysis in a simple undivided electrochemical cell, containing only two current-carrying platinum electrodes. The compounds (A) are reduced and oxidized at the same electrode. If the excitation energy of these compounds is smaller than the potential difference of the reduced ( $A^-$ ) and oxidized ( $A^+$ ) forms, back electron transfer may regenerate the complexes in an electronically excited state ( $A^+ + A^- \rightarrow A^* + A$ ). Under favorable conditions an electrochemiluminescence (ecl) is then observed ( $A^* \rightarrow A + h\nu$ ). A weak ecl appeared upon electrolysis of the following complexes: Ir(III)-(2-phenylpyridine- $C^2, N^1$ ) $_3$ ; [Cu(I)(pyridine)I] $_4$ , Pt(II)(8-quinolinolate) $_2$ , Tb(III)(TTFA) $_3$  (o-phen) $_4$ , with TTFA = thenoyltrifluoroacetate and o-phen = 1.10-phenanthroline, Tb(III)(TTFA) $_4^-$ , and Eu(III)(TTFA) $_3^-$  (o-phen). An ecl of Re(o-phen) $_4$ (CO) $_3$ Cl occurred during the electrolysis of tetralin hydroperoxide in the presence of the rhenium compound. The mechanism of these electrochemical reactions is discussed.

An electrolysis can be considered to be a high-energy process if reduction and oxidation take place at large potential differences. The primary redox products thus formed can participate in a variety of competing processes (1). They may be kinetically labile and undergo fragmentation or substitution reactions. As an alternative a rapid back electron transfer should take place due to the large driving force. This leads to the regeneration of the starting compounds either in the ground state or in an electronically excited state if the potential difference exceeds the excitation energy. At very large driving forces excited state generation is expected to be favored over ground state formation in many cases according to the Marcus theory (2). Various experimental methods are available to gain more insight into such high-energy electron transfer reactions. The detection of excited products is possible if they are luminescent. Chemiluminescence resulting from electron trans-

fer reactions of transition metal complexes has been observed in a few cases (3-14). However, the electrochemical generation of an appropriate redox pair in situ offers various advantages. Under suitable conditions an electrolysis will then be accompanied by light emission (electrochemiluminescence or electrogenerated chemiluminescence, ecl) (15). By application of an alternating current a redox pair is generated at the same electrode.



Back electron transfer takes place from the electrogenerated reductant to the oxidant near the electrode surface. At a sufficient potential difference this annihilation leads to the formation of excited (\*) products which may emit light (ecl) or react "photochemically" without light (1,16). Redox pairs of limited stability can be investigated by ac electrolysis. The frequency of the ac current must be adjusted to the lifetime of the more labile redox partner. Many organic compounds have been shown to undergo ecl (17-19). Much less is known about transition metal complexes despite the fact that they participate in many redox reactions. Most observations of ecl involve  $Ru(bipy)_3^{2+}$  (bipy = 2,2'-bipyridyl) and related complexes which possess emissive charge transfer (CT) metal to ligand (ML) excited states (11,20-33). The organometallic compound  $Re(o\text{-phen})(CO)_3Cl$  (o-phen = 1,10-phenanthroline) is a further example of this category (34). Palladium and platinum porphyrins with emitting intraligand (IL) excited states are also ecl active (35). Under suitable conditions ecl was observed for  $Cr(bipy)_3^{3+}$ . In this case the emission originates from a ligand field (LF) excited state (27). Finally, it has been shown that the electrolysis of  $Pt_2(pop)_4^{2+}$  (36) ( $pop$  = diphosphonate) or  $Mo_6Cl_{12}^{3+}$  (37) is also accompanied by light emission. The redox processes as well as the subsequent excited state formation involve the metal-metal bonding of these polynuclear complexes.

The present investigation was carried out in order to extend ecl to other types of transition metal compounds including organometallics. In addition to the search for new systems the modification of a well-known ecl was used to learn more about the reaction mechanism.

The choice of new complexes was guided by some simple considerations. The overall ecl efficiency of any compound is the product of the photoluminescence quantum yield and the efficiency of excited state formation. This latter parameter is difficult to evaluate. It may be very small depending on many factors. An irreversible decomposition of the primary redox pair can compete with back electron transfer. This back electron transfer could favor the formation of ground state products even if excited state formation is energy sufficient (13,14,38,39). Taking into account these possibilities we selected complexes which show an intense photoluminescence ( $\Phi > 0.01$ ) in order to increase the probability for detection of ecl. In addition, the choice of suitable complexes was also based on the expectation that reduction and oxidation would occur in an appropriate potential range.

### Experimental Section

**Materials.** The compounds  $\text{Re}(\text{o-phen})(\text{CO})_3\text{Cl}$  (40),  $\text{Ir}(\text{2-phenylpyridine-C}^2, \text{N}^1)_3$  (41),  $[\text{Cu}(\text{pyridine})\text{I}]_4$  (42,43),  $\text{Pt}(\text{8-quinolinate})_2$  (44),  $\text{Tb}(\text{TTFA})_3(\text{o-phen})$  (45,46) with  $\text{TTFA}$  = thenoyl-trifluoroacetate,  $[\text{NH}(\text{C}_2\text{H}_5)_3][\text{Tb}(\text{TTFA})_4]$  (45),  $\text{Eu}(\text{TTFA})_3(\text{o-phen})$  (45), and tetralin hydroperoxide (47) were prepared according to published procedures. For the electrochemical experiments acetonitrile and  $\text{CH}_2\text{Cl}_2$  were triple vacuum line distilled from  $\text{P}_4\text{O}_{10}$  and degassed by several freeze-thaw cycles. The supporting electrolyte  $\text{Bu}_4\text{NBF}_4$  was crystallized from dry acetone several times and dried in vacuo.

**Equipment and Methods.** The ac electrolyses were carried out under argon in 1-cm quartz spectrophotometer cells which were equipped with two platinum foil electrodes directly connected to a Kröncke Model 1246 sine wave generator as an ac voltage source. Ecl was detected and spectrally analyzed by several procedures. The first detection was achieved by connecting the spectrophotometer cell directly with a photomultiplier (Hamamatsu 1 P21). This arrangement was also used to obtain maximum ecl intensity by variation of the terminal ac voltage and the ac frequency. A crude spectral analysis of the ecl was accomplished by placing appropriate broad-band interference filters and cut-off filters between the cell and the photomultiplier. The interference filters (Balzer) K3, K4, K5, and K7 transmitted maximum intensity at  $\lambda = 510, 565, 610, \text{ and } 700$  nm. The Schott cut-off filter KV 550 transmitted light of  $\lambda > 530$  nm. Ecl spectra were recorded on a Hitachi 850 Fluorescence Spectrophotometer.

### Results

As reported previously ac electrolyses were carried out in a simple undivided electrochemical cell containing only the two current-carrying electrodes (16). Most compounds investigated in the present study showed only very weak ecl intensities. First experiments were carried out by placing the ecl cell directly in front of a photomultiplier. By this simple procedure the lowest light intensities could be detected. Under comparable experimental conditions integrated ecl intensities were detected which were roughly by a factor of  $10^{-4}$  lower than that of  $\text{Ru}(\text{bipy})_3^{2+}$ . These measurements were used to adjust the experimental parameters such as ac voltage and frequency to maximum ecl intensity. A qualitative analysis of the spectral distribution of ecl was achieved by inserting broad-band interference filters and cut-off glass filters between the cell and the photomultiplier. Finally, complete ecl spectra were recorded on a luminescence spectrometer. Measurements by cyclic voltammetry were carried out by A. Haimerl (48). For the individual compounds the following experimental details of the ecl experiments are given: solvent, concentration of the supporting electrolyte, concentration of the compound subjected to electrolysis, terminal ac voltage, ac frequency, current, integrated ecl intensity in arbitrary units not corrected for photomultiplier response, and wavelength of maximum light intensity, transmitted by appropriate filters.

$\text{Re(o-phen)(CO)}_3\text{Cl}$ .  $\text{CH}_3\text{CN}$ ,  $0.1 \text{ M Bu}_4\text{NBF}_4$ ,  $3 \times 10^{-4} \text{ M}$  complex,  $2 \text{ V}$ ,  $30 \text{ Hz}$ ,  $1.1 \text{ mA}$ ,  $40 \text{ units}$ ,  $\lambda_{\text{max}} = 610 \text{ nm}$ . Upon addition of  $3 \times 10^{-4} \text{ M}$  tetralin hydroperoxide the ecl intensity increased to 120 units.

$\text{Ir(ppy)}_3$  with  $\text{ppy} = 2\text{-phenylpyridine-C}^2, \text{N}^1$ .  $\text{CH}_3\text{CN}$ ,  $0.05 \text{ M Bu}_4\text{NBF}_4$ ,  $10^{-4} \text{ M}$  complex,  $4 \text{ V}$ ,  $10 \text{ Hz}$ ,  $9 \text{ mA}$ ,  $4 \text{ units}$ ,  $\lambda_{\text{max}} = 510 \text{ nm}$ .

$[\text{Cu(py)I}]_4$  with  $\text{py} = \text{pyridine}$ .  $\text{CH}_2\text{Cl}_2$ ,  $0.05 \text{ M Bu}_4\text{NBF}_4$ ,  $2 \times 10^{-4} \text{ M}$  complex,  $5 \text{ V}$ ,  $1 \text{ Hz}$ ,  $10 \text{ mA}$ ,  $20 \text{ units}$ ,  $\lambda_{\text{max}} = 700 \text{ nm}$ .

$\text{Pt(QO)}_2$  with  $\text{QO} = 8\text{-quinolinolate}$ .  $\text{CH}_3\text{CN}$ ,  $0.005 \text{ M Bu}_4\text{NBF}_4$ ,  $3 \times 10^{-4} \text{ M}$  complex,  $4 \text{ V}$ ,  $30 \text{ Hz}$ ,  $8 \text{ mA}$ ,  $10 \text{ units}$ ,  $\lambda_{\text{max}} > 530 \text{ nm}$ ; at  $6 \text{ V}$ ,  $30 \text{ Hz}$ , and  $21 \text{ mA}$  the ecl intensity increased to 200 units.

$\text{Tb(TTFA)}_3(\text{o-phen})$  with  $\text{TTFA} = \text{thenoyltrifluoroacetate}$ .  $\text{CH}_3\text{CN}$ ,  $0.05 \text{ M Bu}_4\text{NBF}_4$ ,  $2.9 \times 10^{-4} \text{ M}$  complex,  $4 \text{ V}$ ,  $300 \text{ Hz}$ ,  $20 \text{ mA}$ ,  $50 \text{ units}$ ,  $\lambda_{\text{max}} = 565 \text{ nm}$ . During electrolysis a solid separates and covers the electrodes.

$[\text{NH}(\text{C}_2\text{H}_5)_3]\text{Tb(TTFA)}_4$ .  $\text{CH}_3\text{CN}$ ,  $0.05 \text{ M Bu}_4\text{NBF}_4$ ,  $3 \times 10^{-4} \text{ M}$  complex,  $4 \text{ V}$ ,  $300 \text{ Hz}$ ,  $20 \text{ mA}$ ,  $2 \text{ units}$ ,  $\lambda_{\text{max}} = 565 \text{ nm}$ .

$\text{Eu(TTFA)}_3(\text{o-phen})$ .  $\text{CH}_3\text{CN}$ ,  $0.005 \text{ M Bu}_4\text{NBF}_4$ ,  $2.7 \times 10^{-4} \text{ M}$  complex,  $4 \text{ V}$ ,  $30 \text{ Hz}$ ,  $8.7 \text{ mA}$ ,  $60 \text{ units}$ ,  $\lambda_{\text{max}} = 610 \text{ nm}$ . Electrodes are covered by a solid during the electrolysis.

## Discussion

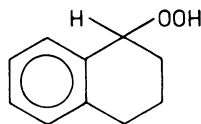
The ac electrolyses of this work were carried out in an undivided electrochemical cell containing only the two current-carrying electrodes. This simple apparatus has certainly its limitations but was appropriate for the detection of new ecl-active compounds. The ecl intensity of most systems studied here was only very small. Generally, there may be several explanations for this observation. In some cases the reduced and oxidized species formed at the electrodes are not very stable as revealed by cyclic voltammetry. Only a small fraction of these reactive molecules may undergo the desired annihilation reaction competing with an irreversible decay. Moreover, the back electron transfer could favor the formation of ground state products even if excited state generation is energy sufficient (13,14,38,39). Finally, for some complexes it is difficult to obtain the materials free of impurities. In other cases the complexes are thermally not completely stable and dissolution is accompanied by a small degree of decomposition. These impurities may either interfere with the desired electrode process or act as quenchers for the excited molecules undergoing ecl.

The main goal of the present study was to discover new ecl-active complexes. But the first example may demonstrate that complexes known to show ecl can serve to gain more insight into the mechanism of electron transfer processes.

Re(o-phen)(CO)<sub>3</sub>Cl and Tetraline Hydroperoxide

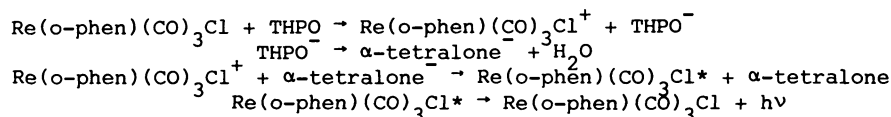
In 1978 Wrighton and his group showed that the complex Re(o-phen)-(CO)<sub>3</sub>Cl undergoes ecl from its lowest excited state which lies about +2.3 eV above the ground state (34). The annihilation is energy sufficient. The oxidation of the neutral complex occurs at  $E_{1/2} = 1.3$  V vs. SCE while the reduction takes place at -1.3 V.

In 1981 we found that Re(o-phen)(CO)<sub>3</sub>Cl shows an intense chemiluminescence during the catalytic decomposition of tetralin hydroperoxide (THPO) in boiling tetraline (12).



THPO

It was suggested that the mechanism of this reaction can be explained on the basis of a "chemically initiated electron exchange luminescence (CIEEL)" (49,50) according to the following scheme:

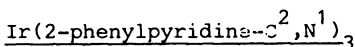


The first step is an activated electron transfer which takes place only at higher temperatures ( $T > 400$  K). In the second step the reduced hydroperoxide is converted to the tetralone anion by elimination of water. This ketyl radical anion is strongly reducing ( $E_{1/2} = -1.12$  V) vs. SCE) (51). Electron transfer to the complex cation provides enough energy ( $\approx 2.4$  eV) to generate Re(o-phen)(CO)<sub>3</sub>Cl in the emitting excited state. The overall process can be described as a catalyzed decomposition of tetralin hydroperoxide. The rhenium complex serves as an electron transfer catalyst which finally takes up the decomposition energy of the peroxide.

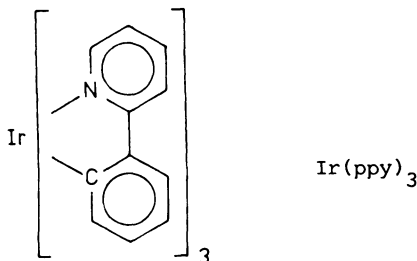
Apparently the same reaction sequence takes place when THPO and Re(o-phen)(CO)<sub>3</sub>Cl are electrolyzed in acetonitrile at room temperature. The electrolysis replaces only the first activated electron transfer step of the CIEEL mechanism.

At an ac frequency of 30 Hz and a voltage larger than 2.6 V the ecl of Re(o-phen)(CO)<sub>3</sub>Cl was very intense. If the voltage dropped below 2.6 V the efficiency of the electrolysis decreased. At 2 V the ecl was very weak. Upon addition of equimolar amounts of THPO the ecl intensity increased by a factor of  $\approx 3$ . The hydroperoxide which is known to undergo an irreversible reduction at  $E_{1/2} = -0.73$  V vs. SCE (52) is apparently reduced during the cathodic cycle while the complex is oxidized during the anodic

cycle. The subsequent reactions are assumed to be the same as those of the CIEEL mechanism. The overall reaction is an electro-catalyzed decomposition of THPO. The complex acts as an electro-catalyst.

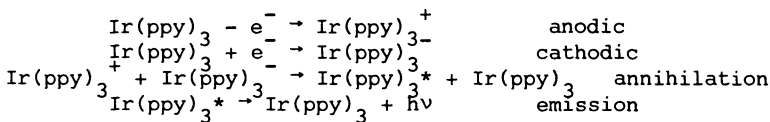


With regard to transition metal complexes the majority of ecl studies have been carried out with  $\text{Ru}(\text{bipy})_3^{2+}$  and its derivatives (11,20-33). Recently, King, Spellane, and Watts reported on the emission properties of  $\text{Ir}(\text{ppy})_3$  with  $\text{ppy} = 2\text{-phenylpyridine-}C^2, N^1$  (41) which can be considered to be an organometallic counterpart of  $\text{Ru}(\text{bipy})_3^{2+}$ .



The lowest excited state ( $\approx 2.5$  eV) of the iridium complex which is also of the MLCT type undergoes an efficient emission. The quantum yield was about 0.4 in deoxygenated toluene at room temperature. The complex can be oxidized at  $E_{1/2} = +0.7$  V vs. SCE. The reduction was not reported but can be estimated to occur at  $E_{1/2} = -1.9$  V. This potential was obtained for the reduction of  $\text{Pt}(\text{ppy})_2$  (53). In this case the reduction was also assumed to take place at the ortho-metalated  $\text{ppy}^-$  ligand.

The potential difference for reduction and oxidation ( $\Delta E \approx 2.6$  V) provides sufficient energy to generate an excited Ir complex in the annihilation reaction. At an ac voltage of 4 V and 10 Hz we observed a weak ecl of  $\text{Ir}(\text{ppy})_3$  in acetonitrile. The following reaction sequence may explain this observation:



Compared to the efficient ecl of  $\text{Ru}(\text{bipy})_3^{2+}$  the low ecl intensity of the Ir complex is rather surprising.

[Cu(pyridine)I]<sub>4</sub>

Binuclear and polynuclear compounds with direct metal-metal interaction constitute a large class of transition metal complexes which play an important role also in organometallic chemistry. Generally, the frontier orbitals of these compounds are engaged in metal-metal bonding. Consequently, redox processes affect the metal-metal interaction. The same is true for the luminescence of such complexes since it involves also the frontier orbitals. The binuclear complex  $\text{Pt}_2(\text{pop})_4$  (36) ( $\text{pop}^-$  = diphosphonate) and the cluster  $\text{Mo}_6\text{Cl}_{12}$  (37) are rare examples of compounds which contain metal-metal bonds and show photoluminescence at ambient conditions. Both complexes are also ecl active. In the present study the tetrameric complex  $[\text{Cu}(\text{py})\text{I}]_4$  with py = pyridine as another compound of this type was investigated.

The colorless tetramer  $[\text{Cu}(\text{py})\text{I}]_4$  is fairly stable only in non- or weakly coordination solvents such as benzene,  $\text{CH}_2\text{Cl}_2$ , or acetone. At room temperature in solution this copper complex shows an intense red photoluminescence ( $\Phi \approx 0.04$ ) at  $\lambda_{\text{max}} = 698 \text{ nm}$  (54). The emitting state is a metal-centered  $3d^4s^1$  excited state which is strongly modified by Cu(I)-Cu(I) interaction in the tetramer. This consists of a  $(\text{CuI})_4$  cubane core.

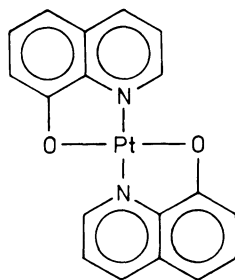
At a terminal voltage of 5 V and a frequency of 1 Hz the complex  $[\text{Cu}(\text{py})\text{I}]_4$  in  $\text{CH}_2\text{Cl}_2$  showed a weak ecl which was clearly identified as the red emission originating from the lowest excited state of the complex.

It seems feasible that the ecl occurs according to the usual mechanism. Reduction and oxidation of the complex is followed by the annihilation and luminescence. However, there must be an efficient competition by other processes since the ecl intensity is rather low compared to the photoluminescence. As indicated by CV measurements the reduction at  $E_{1/2} = -0.7 \text{ V}$  and  $-1.6 \text{ V}$  and oxidation at  $+0.8 \text{ V}$  vs. SCE are largely associated with irreversible reactions. Hence, the reduced and oxidized forms of the complex seem to be not stable. The ecl intensity is then low because only a small fraction of the electrogenerated redox pair escapes an irreversible decay and undergoes an annihilation. It is also possible that the back electron transfer is not quite energy sufficient for the formation of excited  $[\text{Cu}(\text{py})\text{I}]_4^*$  ( $E \approx 2 \text{ eV}$ ) since the potential difference between first reduction and oxidation is only 1.5 V. Finally, the large voltage of 5 V required for the observation of the ecl could also indicate that the solvent  $\text{CH}_2\text{Cl}_2$  which is reduced at  $E_{1/2} = -2.33$  (55) participates in the electrolysis and generation of excited  $[\text{Cu}(\text{py})\text{I}]_4^*$ .

Pt(8-quinolinolate)<sub>2</sub>

The excited states which are responsible for the ecl of the previous examples are of the CTML type or involved in metal-metal bonding of polynuclear complexes. Photoluminescence, or ecl in our case, can also originate from intraligand (IL) excited states provided these states are the lowest excited states of such complexes. IL emissions are characteristic for many transition metal

porphyrins due to the low energy of the  $\pi\pi^*$  transitions of the porphyrin ligand (56). In 1974 Tokel-Takvoryan and Bard observed ecl from porphyrin IL excited states of Pd(II) and Pt(II) tetraphenylporphyrin (35). In the present study we investigated the ecl of  $\text{Pt}(\text{QO})_2$  ( $\text{QO}^- = 8\text{-quinolinolate}$ ) which is associated with an IL state of this Pt(II) chelate.



$\text{Pt}(\text{QO})_2$

In 1978 Scandola and his group observed that solutions of  $\text{Pt}(\text{QO})_2$  exhibit an intense photoluminescence ( $\Phi \approx 0.01$ ) at  $\lambda_{\text{max}} = 650 \text{ nm}$  under ambient conditions (44). More details on the photo-physics and photochemistry of this compound were reported later (57-59). The emitting excited state was assigned to the lowest-energy IL triplet of the chelate ligand.

At a terminal ac voltage of 4 V and a frequency of 30 Hz we observed a weak ecl which was clearly identified as the IL emission of  $\text{Pt}(\text{QO})_2$ . It is assumed that the ac electrolysis generates a redox pair  $\text{Pt}(\text{QO})_2^+/\text{Pt}(\text{QO})_2^-$ . The subsequent annihilation leads to the formation of electronically excited  $\text{Pt}(\text{QO})_2$ . The low ecl intensity may be associated with the observation that the electrochemical oxidation and reduction of  $\text{Pt}(\text{QO})_2$  is largely irreversible. CV measurements revealed an oxidation at  $E_{1/2} = +0.9$  and a reduction at  $-1.7 \text{ V}$  vs. SCE. These redox reactions are probably ligand-based processes. The redox pair generated in the ac electrolysis decays irreversibly to a large extent. Only a small fraction undergoes the annihilation. The potential difference between  $\text{Pt}(\text{QO})_2^+$  and  $\text{Pt}(\text{QO})_2^-$  is 2.6 V. This is certainly sufficient to populate the emitting IL state which lies around 2.0 V above the ground state.

#### Terbium and Europium Complexes

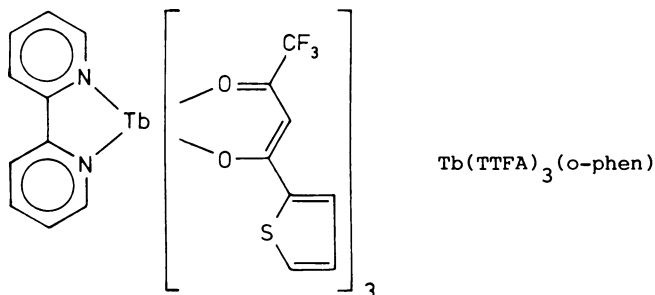
The previous examples of ecl were interpreted on the basis of a relatively simple mechanism. In these cases the back electron transfer generates directly the emitting excited state (annihilation). However, in more complicated systems back electron transfer and formation of an emitting state may be separate processes



(17-19). The back electron transfer leads to a non-emitting excited state which undergoes energy transfer to a luminescent state. This state does not participate in the redox reaction. The energy transfer can occur as an intra- or intermolecular process. An intermolecular sensitization of this type involving a metal complex was studied by Bard and his group (60). An europium chelate served as emitting energy acceptor. In the present work we studied ecl which involves intramolecular energy transfer. The back electron transfer leads to a non-emitting excited state at a certain part of a molecule. Energy transfer populates an emitting excited state at a different part. We selected rare earth metal chelates for this study since they are well known to undergo intramolecular energy transfer from excited IL states to emitting metal-centered f-levels upon IL light absorption (61-64). Moreover, at least Tb(III) is rather redox inert and does certainly not participate in electron transfer processes at moderate potentials.

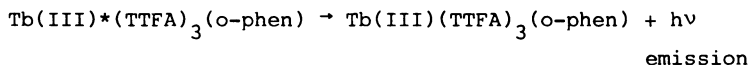
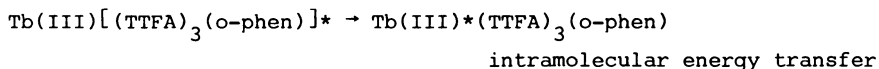
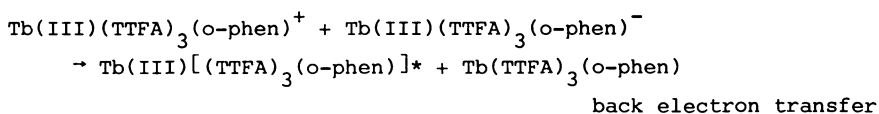
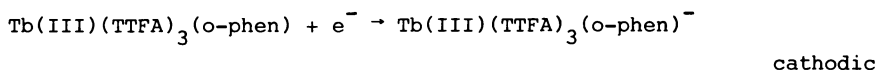
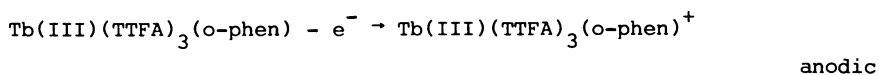
Tb(thenoyltrifluoroacetate)<sub>3</sub>(o-phen)

The complex Tb(TTFA)<sub>3</sub>(o-phen) with TTFA = thenoyltrifluoroacetate is a octacoordinate rare earth chelate which contains one o-phen and three TTFA ligands (45-46). The latter are related to acetylacetonate.



The longest wavelength absorption band of Tb(TTFA)<sub>3</sub>(o-phen) appears at  $\lambda_{\max} = 336$  nm. This intense ( $\epsilon \approx 10^4$ ) and broad band is assigned to an IL transition of TTFA (65). The metal centered f-f bands are all narrow and of low intensity. Light absorption by this IL band caused the typical green emission of Tb(III). The main feature of this structured emission spectrum at  $\lambda_{\max} = 543$  nm is assigned to the  $^5D_4 \rightarrow ^7F_5$  transition of the Tb<sup>3+</sup> ion (63,64). In analogy to many other rare earth chelates an energy transfer occurs from the ligand to the emitting  $^5D_4$  state of Tb<sup>3+</sup> at  $20500 \text{ cm}^{-1}$  or 2.54 eV. The donor state for energy transfer is the lowest TTFA triplet at  $20660 \text{ cm}^{-1}$  or 2.56 eV (63,64).

At a terminal voltage of 4 V and an ac frequency of 300 Hz  $\text{Tb}(\text{TTFA})_3(\text{o-phen})$  showed a weak ecl which was definitely identified as the emission from the  $^5\text{D}_4$  state of  $\text{Tb}(\text{III})$ . The following scheme may describe the ecl mechanism.



The complex  $\text{Tb}(\text{TTFA})_3(\text{o-phen})$  underwent a reduction at  $E_{1/2} = -1.5$  V vs. SCE which was partially reversible. An oxidation was not observed below +2 V. All redox reactions should be ligand-based processes. The potential difference of  $\Delta E > 3.5$  V is energy sufficient to generate the IL triplet at 2.56 eV. The low ecl intensity could be due to a competing irreversible decay of the primary redox pair.

#### $\text{Tb}(\text{thenoyltrifluoroacetate})_4^-$

The absorption ( $\lambda_{\text{max}} = 335$  nm) and emission ( $\lambda_{\text{max}} = 543$  nm) spectrum of  $\text{Tb}(\text{TTFA})_4^-$  are very similar to those of  $\text{Tb}(\text{TTFA})_3(\text{o-phen})$ . The IL excitation of  $\text{Tb}(\text{TTFA})_4^-$  is certainly also followed by energy transfer to the emitting  $^5\text{D}_4$  f-level of  $\text{Tb}(\text{III})$ .

At a terminal voltage of 4 V and a frequency of 300 Hz the anion  $\text{Tb}(\text{TTFA})_4^-$  shows a very weak ecl. It was identified by a broad-band interference filter to appear around 565 nm. The intensity was too low to record the ecl spectrum on the emission spectrometer.

The ecl mechanism is assumed to be the same as that of  $\text{Tb}(\text{TTFA})_3(\text{o-phen})$ . However, the very low ecl intensity of  $\text{Tb}(\text{TTFA})_4^-$  requires an explanation. The first reduction of this anion takes place at  $E_{1/2} = -1.75$  V vs. SCE and is partially

reversible. However, an oxidation at +0.85 V could be due to the free ligand. In solution rare earth complexes are not very stable with regard to loss of ligands. The free ligand interferes then with the redox processes of the complex in the ac electrolysis.

### Eu(thenoyltrifluoroacetate)<sub>3</sub>(o-phen)

In analogy to Tb(III) similar Eu(III) complexes show an intense metal-centered photoluminescence involving the f-levels (61-65). An ecl of an europium(III) chelate was reported before (60). The complex was not involved in the electrolysis. Excited organic compounds formed electrochemically underwent an intermolecular energy transfer to the emitting Eu compound. Interestingly, in the absence of the redox-active organic compounds an ecl of the europium chelate was not observed.

While Tb<sup>3+</sup> is redox inert Eu<sup>3+</sup> can be reduced to Eu<sup>2+</sup> at rather low potentials ( $\approx -0.5$  V) (66,67). This adds a further complication to any possible ecl mechanism involving Eu(III) complexes. Furthermore, the back electron transfer from Eu<sup>2+</sup> to an oxidizing ligand radical generated in the electrolysis is a spin-allowed process if Eu<sup>3+</sup> is formed in its ground state (68). However, the formation of the emitting excited state of Eu<sup>3+</sup> is spin-forbidden. It follows that the generation of Eu<sup>3+</sup> in the ground state could be favored even if the excited state formation is an energy-sufficient process. But it was pointed out that the spin-selection rule may not be important due to the heavy atom effect of europium.

While the absorption spectrum of Eu(TTFA)<sub>3</sub>(o-phen) is nearly identical to that of the corresponding Tb complex, the intense red emission is characteristic for Eu<sup>3+</sup>. The main band of the structured spectrum appears at  $\lambda_{\max} = 613$  nm and is assigned to the metal-centered  $D_0 \rightarrow F_2$  transition (63-65). The emitting  $D_0$  state has an energy of  $17150 \text{ cm}^{-1}$  or 2.13 eV while the lowest IL excited state which is a triplet of the TTFA ligand occurs at  $20450 \text{ cm}^{-1}$  or 2.54 eV. The initially excited ligand undergoes an efficient intramolecular energy transfer to the emitting  $D_0$  state of Eu<sup>3+</sup>.

At a terminal ac voltage of 4 V and a frequency of 30 Hz Eu(TTFA)<sub>3</sub>(o-phen) shows a weak ecl which was identified as the typical emission of Eu<sup>3+</sup> at  $\lambda_{\max} = 613$  nm. Without extensive speculation it is difficult to propose an ecl mechanism due to the complications discussed above.

Eu(TTFA)<sub>3</sub>(o-phen) was not oxidized below +2 V vs. SCE, as indicated by CV measurements. The reduction of Eu<sup>3+</sup> to Eu<sup>2+</sup> is expected to occur around -0.5 V. A clear reduction wave was not observed in this region. Another related Eu(III) chelate (60) was also not reduced near this potential while some Eu(III) cryptates (66,67) undergo a reversible reduction in this range. The complex Eu(TTFA)<sub>3</sub>(o-phen) showed two irreversible reductions at -1.3 and -1.63 V. These are certainly ligand-based processes. The irreversibility may be due to a direct decomposition of the reduced complex. As an alternative the reduced ligand could rapidly transfer an electron to Eu<sup>3+</sup>. The Eu(II) complex may undergo a facile ligand displacement. All these complications at various stages of

the ac electrolysis can contribute to the low ecl intensity of  $\text{Eu}(\text{TTFA})_3(\text{o-phen})$ .

### Conclusion

For transition metal complexes an intense ecl as it was observed for  $\text{Ru}(\text{bipy})_3^{2+}$  seems to be rather an exception. It is certainly difficult to draw definite mechanistic conclusions based on small ecl efficiencies because ecl may originate from side reactions in these cases. However, our results do show that electron transfer reactions with large driving forces can generate electronically excited transition metal complexes as a rather general phenomenon.

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